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(6) **2**; colorless oil; *m/e* 332 (M^+, 23%), 73 (Me_3Si, 100%); NMR τ (C_6D_6) 1.71 (br s, 1 H), 2.53 (br s, 1 H), 5.93 (br d, *J* = 11 Hz, 1 H, –OC*H*H), 6.03 (d, *J* = 9.5 Hz, 1 H, ArC*H*O), 6.62 (ddd, *J* = 13, 11, 2 Hz, 1 H, –OCH*H*), 7.33 (ddd, *J* = 17, 11.5, 6 Hz, 1 H, ArC*H*H), 7.43 (ddd, *J* = 17, 6, 1.5 Hz, 1 H, ArCH*H*), 8.36–9.13 (m, 7 H), 9.61 (s, 18 H, Me_3Si); **6**; colorless crystals, mp 115–116 °C; *m/e* 382 (M^+, 39%), 119 (100%), 73 (Me_3Si, 80%); NMR τ (C_6D_6) 2.34 (s, 1 H, ArH), 2.53 (s, 1 H, Ar*H*), 2.93 (dd, *J* = 8, 7 Hz, 1 H, Ar*H*), 2.99 (dd, *J* = 8, 7 Hz, 1 H, Ar*H*), 3.13 (br dd, *J* = 9, 7 Hz, 2 H, Ar*H*), 4.10 (s, 1 H, ArC*H*O_2), 4.91 (m, 2 H, ArCH_2O), 5.30 (d, 1 H, *J* = 14 Hz, ArC*H*O), 6.96 (d, *J* = 9 Hz, 2 H, ArCH_2), 9.58 (s, 9 H), 9.62 (s, 9 H); **8:** colorless crystals, mp 170–171 °C; *m/e* 411 (M^+, 14%), 73 (Me_3Si, 100%); NMR τ (C_6D_6) 1.63 (s, 1 H, Ar*H*), 2.00 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 2.55 (s, 1 H, Ar*H*), 2.80 (dd, *J* = 9, 8 Hz, 1 H, Ar*H*), 2.94 (dd, *J* = 10.5, 7 Hz, 1 H, Ar*H*), 3.34 (d, *J* = 7 Hz, 1 H, Ar*H*), 4.59 (d, *J* = 10 Hz, 1 H, ArC*H*O), 5.09 (m, 2 H, ArCH_2O), 5.68 (d, *J* = 18 Hz, 1 H, ArC*H*N), 5.82 (d, *J* = 10 Hz, 1 H, ArC*H*N), 5.87 (d, *J* = 18 Hz, 1 H, ArC*H*N), 6.63 (s, 3 H, MeO), 9.56 (s, 9 H), 9.57 (s, 9 H); **13a:** colorless oil; *m/e* 188 (M^+, 84%), 129 (100%); NMR τ (C_6D_6) 2.98 (m, 4 H), 5.95 (dd, *J* = 11, 4 Hz, 1 H, C*H*O), 6.15 (dd, *J* = 11.5, 4 Hz, 1 H, C*H*O), 6.68 (ddd, *J* = 13, 12, 2 Hz, 1 H, C*H*O), 7.03 (dd, *J* = 12, 11 Hz, 1 H, C*H*O), 7.38 (m, 2 H, ArCH_2), 7.82 (br dd, *J* = 12, 12 Hz, 1 H, ArCH_{tert}), 8.13 (br d, *J* = 13 Hz, 1 H, C*H*HCH_2O), 8.52 (m, 2 H), 8.68 (m, 1 H), 8.95 (m, 1 H); **14a**; colorless oil; *m/e* 186 (M^+, 100%), 129 (67%); NMR τ (C_6D_6) 2.75 (d, *J* = 7.5 Hz, 1 H), 2.92 (m, 2 H), 3.00 (d, *J* = 6.5 Hz, 1 H), 7.30 (m, 2 H, ArCH_2), 7.68 (br dd, *J* = 12.5, 3 Hz, 1 H, ArCH_{tert}C*H*H), 7.87 (br dd, *J* = 12, 12 Hz, 1 H, ArCH_{tert}), 8.17–9.08 (m, 10 H).

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(11) Preliminary results indicate useful regioselectivity in electrophilic substitutions of the trimethylsilyl groups.

(12) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

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Structure of Tetrakis(*N*,*N*-diethylmonothiocarbamato)titanium (IV). A Limitation on Orgel's Rule

Sir:

In 1960, Orgel[1] proposed that the π-bonding capabilities of the ligands in eight-coordinate, dodecahedral MX_4Y_4 complexes could determine the manner in which the ligands sort into A and B sites.[2] More specifically, Orgel postulated that in complexes of d^1 and d^2 ions the π-acceptor ligands should occupy the dodecahedral B sites, since the partially or completely filled metal $d_{x^2-y^2}$ orbital is of appropriate symmetry for $d\pi \rightarrow p\pi$ bonding with ligands in the B sites. However, for complexes of d^0 ions π-donor ligands should occupy the B sites so as to facilitate $p\pi \rightarrow d\pi$ interaction involving the vacant metal $d_{x^2-y^2}$ orbital.[3]

While the structures of $[(CH_3NC)_4Mo(CN)_4]$[4] and $[Zr(nes)_4]$[5] (nes = *N*-ethylsalicylaldiminate) tend to support Orgel's proposal, a more definitive test of this idea involves structural comparison of the two closely related complexes $[W(QBr)_4]$[6] and $[ZrQ_4]$[7] (QBr = 5-bromoquinolin-8-olate and Q = quinolin-8-olate); the only important difference between these complexes is the electronic configuration of the metal ion. In the former compound, a d^2 complex, the π-acceptor quinolinolate nitrogen atoms occupy the B sites and the π-donor oxygen atoms occupy the A sites; in the latter compound, a d^0 complex, the site occupancies are reversed, as predicted by Orgel's rule.

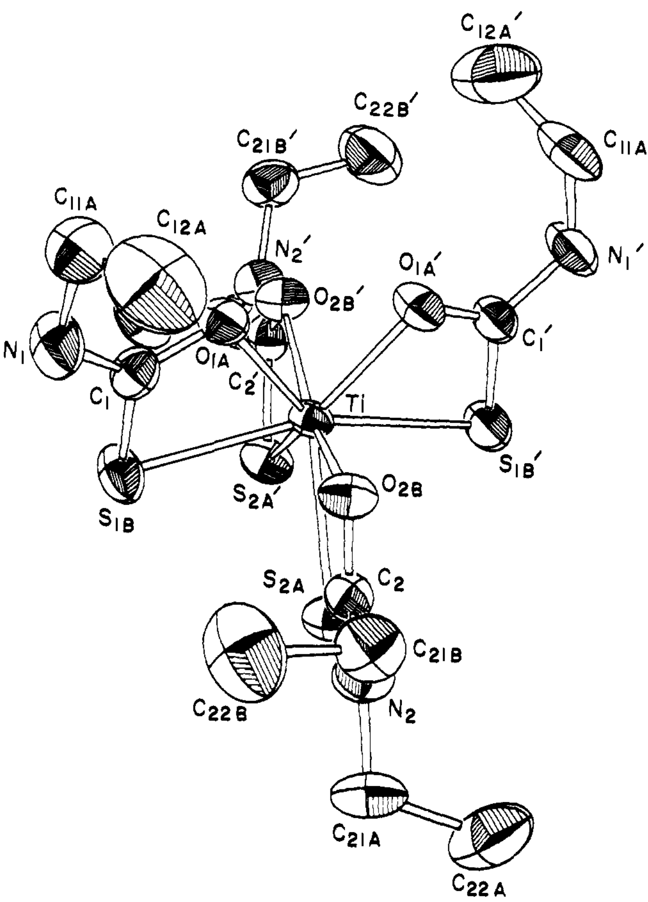

Figure 1. A perspective view of the $[Ti(Et_2mtc)_4]$ molecule. The primed atoms are related to the unprimed atoms by a crystallographic twofold axis. A disordered ethyl group on ligand 1 has been omitted for clarity.

We report herein the synthesis and x-ray structure of the eight-coordinate MX_4Y_4 complex $[Ti(Et_2mtc)_4]$ (Et_2mtc = *N*,*N*-diethylmonothiocarbamate), a complex in which the four sulfur or the four oxygen donor atoms might have been expected to sort into the B sites, depending on the relative π-donor ability of sulfur and oxygen. Instead, the sulfur and oxygen atoms cluster on opposite sides of the molecule so as to give a "cis" arrangement of sulfur atoms.

Air-sensitive, red crystals of composition $Ti(SOCN(C_2H_5)_2)_4$ were isolated following insertion of carbonyl sulfide into the titanium–nitrogen bonds of tetrakis (*N*,*N*-diethylamido)titanium(IV).[8] The compound exhibits a methyl resonance at τ 8.83 and a methylene resonance at τ 6.48 in the ^1H NMR spectrum of a dichloromethane solution at 37 °C. It shows the following characteristic infrared bands: $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, 1547 and 1530; $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, 941; ν(Ti–O), 558; and ν(Ti–S), 320 cm^{-1} (Nujol mull).

Crystal data: $Ti(C_5H_{10}NOS)_4$, mol wt = 576.72; monoclinic, space group $C2/c$ ($C_{2h}{}^6$, No. 15); a = 13.687 (2), b = 13.974 (3), c = 16.990 (4) Å; β = 111.39 (2)°; d_{measd} = 1.267 g cm^{-3}, Z = 4, d_{calcd} = 1.266 g cm^{-3}. The structure was solved by straightforward application of the heavy-atom method and was refined to a final R_1 value of 0.086 and an R_2 value of 0.087 using 3899 observed reflections having $2\theta_{MoK\bar{\alpha}} < 65°$ (the equivalent of 1.6 limiting Cu $K\bar{\alpha}$ spheres) and $|F_o| > 2\sigma(|F_o|)$ measured with a Picker FACS-I automated diffractometer.

Table I. Dimensions of the Dodecahedral Coordination Polyhedron of [Ti(Et$_2$mtc)$_4$]

Bond	Length, Å	Edge type	Atoms	Length, Å
Ti–S$_{1B}$	2.533 (1)	a	O$_{1A}$–O$_{1A}'$	2.491 (6)
Ti–S$_{2A}$	2.609 (1)	a	S$_{2A}$–S$_{2A}'$	3.212 (2)
Ti–O$_{1A}$	2.117 (3)	b	S$_{1B}$–O$_{2B}$	3.205 (3)
Ti–O$_{2B}$	2.061 (3)	b	S$_{1B}$–O$_{2B}'$	3.455 (3)
		m	S$_{1B}$–O$_{1A}$	2.530 (3)
		m	S$_{2A}$–O$_{2B}$	2.540 (3)
		g	S$_{1B}$–S$_{2A}$	3.327 (2)
		g	S$_{1B}$–S$_{2A}'$	3.367 (2)
		g	O$_{1A}$–O$_{2B}$	2.662 (4)
		g	O$_{1A}$–O$_{2B}'$	2.701 (4)

The geometry of the complex (see Figure 1) is best described in terms of a slightly distorted dodecahedral coordination polyhedron with the bidentate monothiocarbamate ligands spanning *m* edges to give the *mmmm* stereoisomer.[2] The titanium atom is located on a crystallographic twofold axis which is coincident with the $\bar{4}$ axis of the idealized $D_{2d} - \bar{4}2m$ dodecahedron. The interpenetrating ABBA trapezoids are nearly perpendicular (dihedral angle = 87.4°) with the titanium atom and the four donor atoms which define an individual trapezoid being planar to within 0.06 Å. Other measures of the extent to which the coordination polyhedron approximates the idealized dodecahedron are the δ and ϕ shape parameters defined by Porai-Koshits and Aslanov.[11] The δ parameters for eight-atom geometries are 29.5° for the D_{2d} dodecahedron; 0.0, 21.8, and 48.2° for the C_{2v} bicapped trigonal prism; and 0.0 and 52.4° for the D_{4d} square antiprism; the ϕ parameters for the three idealized geometries are 0.0, 14.1, and 24.5°, respectively. For [Ti(Et$_2$mtc)$_4$] the two independent δ parameters are 26.3 and 34.8°, while the ϕ parameters are 3.6 and 3.8°, values which again indicate that the coordination polyhedron of [Ti(Et$_2$mtc)$_4$] most closely approximates a dodecahedron.

Metal–ligand bond distances and polyhedral edge lengths are listed in Table I. As is expected for molecules of this geometry,[2] complexing bonds to the dodecahedral B sites are shorter than bonds to the A sites (by 0.076 and 0.056 Å for Ti–S and Ti–O, respectively).

The most interesting feature of the structure is that the sulfur and oxygen atoms do *not* sort between the A and B sites as suggested by Orgel's rule, but rather partially sort so that half of the sulfur atoms are in A sites and the other half are in B sites. Thus the molecule is a pseudo-C_{2v} stereoisomer instead of one of the two possible D_{2d} stereoisomers in which the donor atoms are completely sorted. Although no one of the three stereoisomers appears to be sterically favored over the other two, the observed stereoisomer has five relatively short (3.212–3.367 Å) S···S contacts, while the D_{2d} stereoisomer with sulfur atoms in A sites would have only two short S···S contacts and the D_{2d} stereoisomer with sulfur atoms in B sites would have four long S···S contacts. This result suggests that the donor atom sorting pattern in [Ti(Et$_2$mtc)$_4$] may be determined by weakly attractive S···S interactions. Weak interligand bonding between sulfur atoms has been suggested previously for trigonal prismatic tris(1,2-dithiolene) complexes[12,13] and may be important in the preference for cis stereochemistry in octahedral[14] and square planar[15-21] β-thioketonate complexes. Note that [Ti(Et$_2$dtc)$_4$] also has cis stereochemistry in that all four sulfur atoms are located on one side of the molecule and all four oxygen atoms are found on the other side.

Although Orgel's proposal may be useful in predicting the stereochemistry of some eight-coordinate dodecahedral complexes, the structure of [Ti(Et$_2$mtc)$_4$] indicates that the stereoisomer observed may be determined by factors other than the electronic configuration of the metal atom and the π-bonding capabilities of the ligands, in this case the postulated weak, attractive S···S interactions.[22]

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Reaction of Strained Acetylenes with Molecular Oxygen. A Novel Chemiluminescent Reaction, Evidence for a Dioxetene, and a Mechanism for Thermal Generation of Singlet Oxygen

Sir:

The cyclic seven-membered ring acetylene **1** possesses an exceptionally small[1] C—C≡C bond angle of 146°. The two π orbitals of **1** are not degenerate, but are split into a higher energy orbital which is roughly in the molecular plane (π_y) and a lower energy orbital[2] which is perpendicular to the molecular plane (π_z). **1** reacts in the dark with atmospheric oxygen to produce the dione **2** (eq 1) in good yield.[3] Successful cycloaddition reactions of singlet oxygen to acetylenes are rare.[4] Importantly, reaction 1 involves triplet oxygen, so that at some stage along the pathway to **2**, a triplet-singlet intersystem crossing must occur. We report here a detailed investigation of reaction 1.

Heating (~90°) of an oxygen saturated solution of **1** in